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(54) COMPOSITE CATALYST AND DISPROPORTIONATION OF ALKYL BENZENES

(71) We, TEXACO DEVELOPMENT CORPORATION, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of 135 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel catalyst, to a method for preparing the catalyst, and to the catalytic conversion of alkylaromatic hydrocarbons using the catalyst. In a particularly desirable embodiment this invention is directed to the catalytic disproportionation of alkylaromatic hydrocarbons such as toluene, xylene, trimethylbenzenes, tetramethylbenzenes and pentamethylbenzenes. In addition, disproportionation can be accomplished by isomerization and transalkylation. In another embodiment, the catalyst according to the invention is employed for the selective catalytic disproportionation of such alkylbenzenes as ethylbenzene, cumene and n-propylbenzene to benzene and dialkylbenzenes.

The catalytic conversion of alkylbenzenes has heretofore been considered employing a variety of catalysts. Catalysts proposed by the art include hydrogen mordenites containing a sulphided Group VIII metal and particularly decationized or hydrogen mordenites having high silica to alumina ratios as disclosed in U.S. Patent No. 3,476,821. The process and catalytic compositions disclosed in this reference provide numerous advantages, including the ability to convert toluene selectively into benzene and xylenes, with virtually no naphthene formation. While, however, the known catalysts and processes provide some degree of disproportionation of non-methyl alkylbenzenes to dialkylbenzenes the degree of conversion is limited, or undesirable amounts of trialkylbenzenes were formed. Further investi-

gation has now shown that such processes and catalysts can be further upgraded, leading to higher conversion of the alkylaromatic hydrocarbons and increased yields of desired products, as well as effectively improving the physical characteristics of the catalysts.

This invention provides a composite catalyst which comprises

(a) hydrogen mordenite having a silica to alumina mole ratio of from 12:1 to 80:1, said hydrogen mordenite being impregnated with

(b) a sulphided metal from Group VIII of the Mendeleev Periodic Table, and

(c) said composite catalyst comprising from 10 to 50 weight % of an eta-alumina or gamma-alumina binder.

This invention furthermore provides a method of preparing the catalyst which comprises

(a) impregnating said hydrogen mordenite with a Group VIII metal;

(b) admixing said impregnated mordenite with hydrated alumina;

(c) calcining the resulting mixture at a temperature up to 1100°F thereby converting said hydrated alumina into an eta-alumina or gamma-alumina binder; and

(d) sulphiding said Group VIII metal.

The invention further provides a process for the conversion of alkylaromatic hydrocarbons which comprises contacting said hydrocarbon with a sulphide compound and a composite catalyst as defined above. It has been found that the conversion of alkylaromatic hydrocarbons in the presence of the aforementioned catalyst is significantly improved, and that the catalyst compositions according to the invention possess superior mechanical strength, contributing to long catalyst life under the processing conditions.

The contemplated alkylaromatic conversion process described in greater detail below, involves disproportionation of the named hydrocarbons. As additional embodiments of the process, disproportionation can also be accom-

panied by isomerization and/or transalkylation of the hydrocarbon feedstock.

The alkylaromatic hydrocarbons which can be converted by the process according to the invention include alkylbenzenes possessing from one to five methyl groups. Particularly preferred alkylbenzenes are those containing from 1 to 4 methyl groups, where the feedstock can be any of the methylated aromatic hydrocarbons or mixtures thereof. Specific examples include toluene; *ortho*-, *meta*- and *para*-xylene; trimethylbenzenes such as mesitylene, pseudocumene and hemimellitene; tetramethylbenzenes including durene, isodurene and prehnitene; and pentamethylbenzene along with mixtures of the above.

Another group of hydrocarbons that can be disproportionated by the process according to the invention include non-methyl alkylbenzenes corresponding to the formula:



where R is an alkyl group of from 2 to 16, preferably 2 to 4, carbon atoms. Specific examples of these alkylbenzenes are ethylbenzene, cumene, *n*-propylbenzene, *t*-butylbenzene, a mixture of *n*-propyl- and isopropylbenzene, *n*-hexylbenzene, 2-*n*-hexylbenzene, isooctylbenzene, *n*-decylbenzene, *n*-dodecylbenzene, 3-*n*-dodecylbenzene and *n*-hexadecylbenzene. Mixtures of these alkylbenzenes can also be disproportionated, the preferred mixtures being those of compounds having a like number of carbon atoms in the alkyl group. Individually preferred alkylbenzenes are ethylbenzene, cumene and *t*-butylbenzene.

With regard to the conversion of the hydrocarbon by means of disproportionation, the feedstock containing one or more alkylaromatic hydrocarbons is contacted with the aforementioned catalyst at a temperature effective to convert at least some of the alkylaromatic hydrocarbons into aromatic products having a greater number and into those having a lesser number of carbon atoms.

In addition to hydrocarbons undergoing disproportionation, hydrocarbons isomerized by the present process include those alkylbenzenes possessing from two to four methyl groups including *ortho*-, *meta*- and *para*-xylene, trimethylbenzenes such as mesitylene, pseudocumene and hemimellitene and tetramethylbenzenes such as durene, isodurene and prehnitene, along with mixtures of the above.

Likewise, disproportionation can be associated with transalkylation when the feedstock comprises a mixture of at least two alkylbenzenes having from one to five methyl groups and where at least two alkylbenzenes in the

mixture have a different number of methyl groups. Illustratively, toluene and pentamethylbenzene can be transalkylated to xylenes, trimethylbenzenes and tetramethylbenzenes.

Similarly, disproportionation, isomerization and transalkylation can be simultaneously undertaken when the feedstock comprises a mixture of at least two alkylbenzenes having from two to four methyl groups, and where at least two alkylbenzenes in the mixture have a different number of methyl groups. For example, such a conversion can be conducted employing a mixture of a xylene, such as *ortho*-xylene, and 1,2,4,5-tetramethylbenzene.

In accordance with our invention, the composite catalyst employed to convert the aforementioned hydrocarbons is prepared by initially providing a hydrogen mordenite having a silica to alumina mole ratio from 12:1 to 80:1. In a highly preferred embodiment the hydrogen mordenite has a silica to alumina mole ratio of 25:1 to 50:1. Hydrogen mordenites for use as a component of the composite catalyst can be prepared from natural or commercially available synthetic sodium mordenites or commercially available hydrogen mordenites having silica to alumina ratios of about 10:1.

The sodium form of mordenite is not effective as a component of the catalyst employed herein. It may, however, be converted into hydrogen mordenite by ion exchange of the sodium in the mordenite with ammonium ions, followed by heating or calcining to drive off ammonia. Alternatively, decationized or hydrogen mordenite can be provided by acid treatment of the sodium form. The hydrogen mordenite (10:1 SiO₂/Al₂O₃), whether prepared as above or available from commercial sources, is thereafter subjected to severe acid leaching so as to increase the silica to alumina mole ratio of the hydrogen mordenite to the required range from 12:1 to 80:1. The acid leaching operation must not, however, destroy the crystalline structure of the mordenite. Moreover, little improvement is realized in the process when the silica to alumina ratio of the mordenite exceeds the required range. Consequently, as a practical limit the acid leaching should be severe enough to produce a mordenite having a silica to alumina ratio of from 12:1 to 80:1, preferably from 25:1 to 50:1. To acid-leach the hydrogen mordenite, a mineral acid, for example hydrochloric or sulphuric acid, is employed to remove aluminium selectively without destroying the crystalline structure of the mordenite. Acid strengths of 1 to 8N are appropriate, and the leaching temperatures can range from room temperature up to the boiling point of the acid solution. Acid-leaching is best accomplished when the mordenite is in the powdered form and not when pelleted. Following the leaching operation, the mordenite is water

washed free of acid anions and is in the form of small soft aggregates, generally of a particle size in the range of 0.5 to 10 microns.

The acid-leached hydrogen mordenite is now in a suitable form for impregnation with an aqueous solution of a Group VIII metal salt. Group VIB metals may also be associated with the mordenite, and the Group VIII impregnating solution may additionally contain soluble salts of members of Group VIB, or separate and subsequent impregnation may be undertaken with the Group VIB component. Group VIII metals including platinum, palladium, rhodium, ruthenium, nickel and cobalt are introduced in an amount sufficient to provide the final composite catalyst with a Group VIII metal content of from 0.2 to 10.0 weight %. Preferably, nickel or cobalt are employed in an amount of from 3.0 to 8.0 weight %. Platinum, palladium, rhodium and ruthenium are preferably present in an amount of 0.2 to 2.0 weight %. The Group VIB metal, i.e. tungsten, molybdenum or chromium, can also be associated with the hydrogen mordenite in an amount of from 3.0 to 15.0 weight % based on the composite catalyst. After employing impregnation techniques well known to the art, the impregnated high-silica hydrogen mordenite is beneficially heated to a temperature of from 100 to 300°F so as partially to dry the impregnated particles.

The improvements in alkylaromatic conversion are achieved by mixing the metal-impregnated high-silica hydrogen mordenite with hydrated alumina, such that the ultimate composite catalyst contains alumina as a component thereof in an amount of from 10 to 50 weight %, preferably from 15 to 30 weight %. In practice, the metal-impregnated mordenite is introduced into a freshly prepared precipitate of hydrated alumina, such as alpha- or beta - alumina hydrate, and the components are milled by passing through a Colloid Mill to give a uniform dispersion of the mordenite in the alumina. The mixing in the Colloid Mill causes the impregnated mordenite aggregates, some of which may be of a size of 20 to 50 microns, to be broken down into particles having average diameters of 0.5 to 5 microns. It has been found that by impregnating the hydrogen mordenite powder, it is possible to secure a more uniform distribution of the metal component than can be obtained by impregnation of a formed pellet. The composite resulting from the mixing operation is dried, for example at the temperatures of 130 to 150°F, although higher or lower temperatures may also be employed. The composite is subsequently crushed and sieved, for example through a -40 mesh (US Standard). Sufficient water is added to give a good extrusion mix and the composite is formed into the desired shape contemplated for ultimate use. Illustratively, the particles

can be ground to provide a finely divided catalytic mass, for instance by mulling, or beads may be formed, but it is preferred that the composite be extruded.

Subsequent to shaping, the composite is dried and calcined at a temperature of up to 1100°F. Drying of the composite may be undertaken at ambient temperature, or at temperatures of about 300°F, for several hours. Alternatively, ambient temperature can be initially employed with subsequent incremental increases in temperature to about 300°F. Thereafter the composite is calcined at temperatures of from 500 to 1100°F, preferably in a stream of dry gas, and preferably at maximum temperatures of from 850 to 1000°F. Calcining of the composite converts the hydrated alumina into a gamma- or eta-alumina binder, depending upon whether the initial hydrate with alpha- or beta-alumina. At the completion of the calcination step, the converted alumina is transformed into a strong binder. Pellets prepared by this technique possess crush strengths of from 10 to 40 pounds, whereas catalysts excluding alumina are weak and have crush strengths of only a few pounds.

The Group VIII metal component of the calcined composite is thereafter converted into the sulphide and maintained in that condition during use. The metal component may be sulphided by contacting with for example hydrogen sulphide, at a temperature of from 400 to 800°F, contained in a carrier gas such as hydrogen. In another technique the catalyst can be heated to operating temperature and then contacted with the liquid free enriched with a sulphur-containing compound, for example carbon disulphide or dimethyl disulphide.

Inasmuch as the sulphided catalyst metal may be reduced during use, particularly when alkylaromatic conversion is conducted in the presence of hydrogen, the introduction of minor amounts of sulphur compounds into the reaction vessel will maintain the catalyst in a sulphided condition. This may be done by adding hydrogen sulphide to the hydrogen stream entering the reactor, or by incorporating compounds, such as carbon disulphide or dimethyl disulphide, which decompose readily to hydrogen sulphide in the presence of hydrogen under the reactor conditions. These additions should be sufficient to maintain a mole ratio of hydrogen sulphide to hydrogen in the gas phase of from 3×10^{-4} to 1×10^{-2} over the catalyst. Typically, mole ratios of from 7×10^{-4} to 5×10^{-2} of hydrogen sulphide to hydrogen are used, with the higher ratios of $H_2S:H_2$ generally being used at higher reaction temperatures. It has been found that this low concentration of sulphide achieves the desired result without contaminating the products of conversion.

Although hydrogen has often been employed

in prior art catalytic conversion processes, its use in the process of the present invention is not critical. The use of hydrogen is recommended, however, since it will prolong the useful life of the catalyst. In general preferred operating conditions for alkylaromatic conversion, when the alkylaromatic hydrocarbon is a methyl-substituted benzene, include space velocities in the range of 0.1 to 15 liquid volumes per hour per volume of catalyst, preferably 0.5 to 8 LHSV; temperatures in the range of 400 to 750°F, preferably 450 to 650°F; pressures within the range of 100 to 2000 p.s.i.g., preferably in the range of 800 to 1200 p.s.i.g.; and, when hydrogen is used, hydrogen concentrations of 100 to 15,000 s.c.f./bbl. of feed, preferably 5000 to 10,000 s.c.f./bbl. The reaction is suitably carried out over a fixed bed of catalyst with feedstock passing downwardly through the catalyst bed.

When the catalysts are employed for the disproportionation of alkylbenzenes in which the alkyl groups have 2 to 16 carbon atoms, the operating conditions are generally the same, except that the temperatures employed are advantageously from 350 to 650°F, preferably from 450 to 600°F, for ethylbenzene and cumene, and 400 to 550°C for compounds containing butyl and higher alkyl groups.

As the catalyst ages, its activity slowly diminishes. The catalyst may be maintained at or periodically brought back to, approximately its initial level of activity by increasing the operating temperature. Ultimately, regeneration of the catalyst by oxidation can be employed, involving a controlled burning of the contaminants from the surface of the catalyst structure with air, or a mixture of inert gases with air or oxygen.

The beneficial effects derived from the aforementioned invention are twofold. First the composite catalyst possesses significantly greater mechanical strength than dealuminized mordenites containing a sulphided Group VIII metal thereon. The improved mechanical strength is attributed to the presence in the composite of the eta- or gamma-alumina binder. Secondly, and totally unexpected, is the greater activity possessed by the composite catalyst containing the alumina binder. Such a result was unexpected, inasmuch as alumina is virtually an inert material for disproportionating alkylbenzenes. Contrary to what would have been expected, namely that the catalyst activity of the Group VIII sulphided de-aluminized mordenite would be diminished by dilution with alumina, it has been found that higher conversions, in terms of alkylbenzene converted, result in the presence of the composite catalyst.

Operating in accordance with the conditions and catalyst described above, it has been found that a methylated aromatic feedstock is selectively converted into products which are substantially free of ethylated aromatics, C₆

and C₇ naphthenes and light hydrocracked products boiling below 150°F. For example, toluene disproportionates to benzene and isomeric xylenes, yielding a product substantially free of ethylbenzene, thereby providing an attractive route for the preparation and recovery of *para*-xylene from the C₈ aromatic fractions formed. Likewise, disproportionation of *ortho*-xylene results in a product low in alkylated aromatic isomer content such that the concentration of trimethylbenzenes is proportionately high and recovery of mesitylene, in particular, by distillation is facilitated by the relative absence of ethyltoluenes such as *ortho*-ethyltoluene. Other advantages include the absence of ethylbenzene in the xylene fraction enabling recovery of *para*-xylene by low temperature crystallization more efficiently. The disproportionation of xylene or more highly methylated benzenes leads to isomerization of the C₈, C₉, and C₁₀ methylbenzenes to approximately their thermodynamic equilibrium distribution.

On disproportionating and isomerizing *ortho*-xylene, pseudocumene and other polymethylbenzenes, the relative amounts of the dimethyl-, trimethyl- and tetramethylbenzene isomers are approximately in accordance with the amounts anticipated from thermodynamic considerations. For example, the relative amounts of dimethylbenzenes, trimethylbenzenes and tetramethylbenzenes to be found in the C₈, C₉ and C₁₀ fractions respectively, from thermodynamic equilibrium considerations, are as follows at 441°F and 621°F.

Temperature, °F	441	621
Mole Percent in C ₈ fraction		
1,2 - dimethylbenzene	20.6	21.9
1,3 - dimethylbenzene	55.2	54.1
1,4 - dimethylbenzene	24.2	24.0
Mole Percent in C ₉ fraction		
1,2,3 - trimethylbenzene	6.0	7.7
1,2,4 - trimethylbenzene	67.1	67.8
1,3,5 - trimethylbenzene	26.9	24.5
Mole Percent in C ₁₀ fraction		
1,2,3,4 - tetramethylbenzene	13.1	15.2
1,2,3,5 - tetramethylbenzene	51.3	50.5
1,2,4,5 - tetramethylbenzene	35.6	34.3

As will be seen in the Examples below, the relative amounts of the dimethylbenzenes and trimethylbenzenes on isomerizing and disproportionating xylene are in good agreement with these thermodynamic values. In disproportionating pseudocumene (1,2,4 - trimethylbenzene), the amount of prehnitene (1,2,3,4-tetramethylbenzene) relative to the other tetramethylbenzenes is slightly less and the amount of durene (1,2,4,5 - tetramethylbenzene) is

slightly greater than the amounts predicted on chemical equilibrium considerations. The formation of a greater amount of durene relative to prehnitene than would be expected from thermodynamic considerations is a desirable result, as durene is a more valuable material and its recovery is favoured by higher contents in the C_{10} fraction.

It has also been found that ethylbenzene disproportionates forming *meta*-, *para*- and *ortho*-diethylbenzenes, with no other material boiling near these ingredients. The relative amounts of the *para*-, *meta*- and *ortho*-isomers are approximately those expected from thermodynamic equilibrium considerations, and the ratios are those obtained with other types of catalysts.

Small amounts of triethylbenzenes are also formed during disproportionation of ethylbenzene. However, unlike results obtained with zeolite Y catalysts, where the ratio of 1,3,5- to 1,2,4-triethylbenzene corresponds to the thermodynamic ratio of 2:1, the ratio of 1,3,5- to 1,2,4-triethylbenzene is found to be well below 2 for the high SiO_2/Al_2O_3 mole ratio acid mordenite composite catalyst of the present invention.

When disproportionating cumene, the di-isopropylbenzenes and benzene are the predominant products, with little tri-isopropylbenzene being formed. The di-isopropylbenzenes are formed in a ratio similar to that found with other catalysts. However, the ratio of 1,3,5- to 1,2,4-tri-isopropylbenzene formed with the high SiO_2/Al_2O_3 mole ratio acid mordenite composite catalyst is well below the value expected for tri-isopropylbenzenes.

Similarly, the total amounts of trialkylbenzenes (1,3,5- and 1,2,4-trialkylbenzenes) are less than those obtained with other catalysts for the same degree of non-methyl alkylbenzene disproportionation. The disproportionation is primarily limited to benzene and dialkylbenzene formation, and secondary disproportionation of the dialkylbenzenes is suppressed. This suggests that the composite catalysts according to the invention act as shape-selective catalysts.

The disproportionated and isomerized aromatic hydrocarbons provided by process of the invention have utility as solvents or as raw materials for the manufacture of numerous industrial chemicals and products. For example *ortho*-xylene finds application as a raw material in the production of phthalic anhydride and phthalate plasticizers, while *meta*-xylene is important in the production of isophthalic acid. *Para*-xylene is used in the production of terephthalic acid or terephthalate esters, which find particular utility in the manufacture of polyester fibre. Benzene produced in the process is useful as a solvent and as a raw material for the synthesis of styrene, phenol, nitrobenzene and cyclohexane, which

in turn can be used to produce such materials as synthetic rubber, detergents, and insecticides. Other aromatic hydrocarbons, such as the trimethylbenzenes, pseudocumene and mesitylene are employed respectively to prepare trimetallitic anhydride, useful in preparing non-volatile plasticizers and trimesic acid to make cross-linked polymers. Tetramethylbenzenes such as durene are employed in making pyromellitic dianhydride used in the preparation of higher temperature resistant polymers.

Diethylbenzenes may be separated by chromatographic adsorptive processes and thereafter dehydrogenated to divinylbenzene, a polymer precursor. Likewise, *para*-di-isopropylbenzene may be dehydrogenated to *para*-di-isopropylbenzene, a polymer precursor. The *ortho*-, *meta*-, and *para*-di-isopropylbenzenes are also valuable in preparing catechol, resorcinol and hydroquinone respectively, by oxidizing the di-isopropylbenzene to the corresponding dihydroperoxide which is cleaved to the dihydroxybenzene and acetone.

In order to illustrate more fully the nature of this invention and the manner in which it can be practised the following examples are presented. All mesh sizes are U.S. Standard Mesh.

EXAMPLE 1

2000 grams of a commercially available sodium mordenite powder having an average particle size of 10 to 30 microns and comprising 6.86 weight % of Na_2O , 10.2 weight % of Al_2O_3 , and 68.2 weight % of SiO_2 and having a SiO_2/Al_2O_3 mole ratio of 11.4/1 was acid-leached with 4 litres of 6N HCl for 24 hours at a temperature of 130 to 140°F. The acid was decanted and the solids were washed three times with 4 litres of hot water and three times with 4 litres of cold water, giving a product comprising 0.95 weight % of Na_2O , 6.9 weight % of Al_2O_3 , and 86.1 weight % of SiO_2 , and having a SiO_2/Al_2O_3 mole ratio of 21.2/1. The acid-leaching was again repeated, and the product was washed free of chloride ion, dried at 300°F and calcined at a temperature of 1000°F in a stream of dry air. The final acid-leached mordenite consisted of 0.09 weight % of Na_2O , 3.74 weight % of Al_2O_3 , and 88.2 weight % of SiO_2 , and had a SiO_2/Al_2O_3 mole ratio of 40/1.

410 grams of the acid-leached mordenite were impregnated with 250 cc of a cobalt nitrate solution containing 125 grams of $Co(NO_3)_2 \cdot 6H_2O$, and the impregnated powder was dried for 16 hours at a temperature of 130 to 140°F.

368 grams of $Al_2(SO_4)_3 \cdot 18H_2O$ were dissolved in 3 litres of distilled water, and 300 cc of concentrated ammonium hydroxide were added to precipitate aluminium hydroxide. The precipitate was recovered by

filtration and washed 3 times with distilled water. The cobalt-impregnated acid-leached mordenite was mixed with the wet hydrated alumina precipitate and passed through a mill to effect homogeneous mixing. After partially drying the mixture at a temperature of 130 to 140°F for 16 hours and extruding into 1/16 inch pellets, the pellets were dried at room temperature for 16 hours, at 130 to 140°F for 8 hours, at 300°F for 16 hours and finally calcined at 1000°F for 2 hours in dry air. The calcined catalyst pellets were sulphided at 700°F for 4 hours with hydrogen sulphide. The recovered sulphided catalyst

comprised 4.4 weight % of cobalt, 6 weight % of sulphur, and 15 weight % of gamma-alumina, the remainder being hydrogen mordenite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 40/1. The composite catalyst had an average crush strength of 20 pounds as determined by using a Chatillon Crush Strength Tester.

A series of runs was conducted using a toluene feedstock comprising 99.8 weight % of toluene and 0.2 weight % of carbon disulphide, which was introduced to disproportionation reactors containing 100 cc of the catalyst prepared above under the processing conditions summarized in Table I.

TABLE I

Run	1	2	3
Temperature, °F	550	515	575
LHSV	2.0	5.3	4.9
Pressure, p.s.i.g.	800	800	800
H ₂ /hydrocarbon mole ratio	5	5	5
Weight % Sulphur in Feed	0.2	0.2	0.2
Product Analysis, wt. %			
Cracked Below C ₆	0.06	—	—
C ₆ , C ₇ , C ₈ naphthenes	0.19	0.05	0.08
Benzene	22.64	9.77	17.77
Toluene	49.12	78.23	59.82
Ethylbenzene	0.09	8.66	15.27
Para - xylene	5.87		
Meta - xylene	12.96		
Ortho - xylene	4.89	2.26	4.13
Para - ethyltoluene	0.08	0.07	0.22
Meta-+ortho - ethyltoluene	0.20		
Mesitylene	1.10	0.26	0.72
Pseudocumene	2.33	0.62	1.62
Hemimellitene	0.30	0.07	0.21
Ethylxylenes	0.04	—	0.03
Durene	0.05	0.01	0.05
Isodurene	0.05		0.04
Prehnitene	0.02	—	0.02
Heavier than C ₁₀	0.01	—	0.02

In the temperature range of 500 to 600°F the maximum theoretical conversion of toluene by disproportionation is about 58%. It is seen from Table I that an approach of about 87% to chemical equilibrium is obtained at 550°F and 2 LHSV, while at the same time a high selectivity for benzene and polymethylbenzene formation is retained. For example, the C₈ aromatic fraction is nearly all dimethylbenzenes (xylenes) with less than 0.4% of ethylbenzene. This C₈ fraction is then an excellent stock for xylene separation, as there is no need to fractionate out ethylbenzene before para - xylene recovery can be initiated. The xylene concentrations in the C₈ aromatic fraction are at thermodynamic equilibrium with each other, and the same is true of the trimethylbenzenes in the C₉ fraction.

Significant conversions are also obtained at still higher flow rates of toluene over the

catalyst and at temperatures of 515 and 575°F.

EXAMPLE 2

2000 grams of the commercially available sodium mordenite powder used in Example 1 were acid-leached four times under the conditions set out in Example 1. The final acid-leached mordenite comprised 0.02 weight % of Na₂O, 2.54 weight % of Al₂O₃, and 90.6 weight % of SiO₂, and had a SiO₂/Al₂O₃ mole ratio of 60/1.

400 grams of the above described acid-leached mordenite was impregnated with 200 cc of a nickel nitrate solution containing 107 grams of Ni(NO₃)₂ · 6H₂O and the impregnated powder was dried for 16 hours at a temperature of 130 to 140°F.

817 grams of Al₂(SO₄)₃ · 18H₂O were dissolved in 3 litres of distilled water, and

400 cc of concentrated ammonium hydroxide were added to precipitate aluminium hydroxide. The precipitate was recovered by filtration and washed three times with distilled water. Half of the resulting alumina gel was used in further preparing the catalyst.

720 grams of the nickel-impregnated acid-leached mordenite were mixed with 1455 grams of wet hydrated alumina gel and passed through a mill to effect homogeneous mixing. After partially drying the mixture at 130 and 140°F for 16 hours the mixture was ground and sieved to -40 mesh. Sufficient water was added to ensure a good extrusion mix and the material was then extruded into 1/16 inch pellets. The pellets were dried at ambient temperature for 16 hours, at 130 to 140°F for 8 hours, and at 300°F for 16 hours. Thereafter, the pellets were calcined in dry air starting at 500°F, and the temperature was raised in increments of 100°F per hour until a final temperature of 1000°F was reached, whereupon the catalyst was calcined at 1000°F for two hours in dry air.

The calcined catalyst was sulphided at 700°F for 4 hours with H_2S and subsequently cooled in a stream of dry nitrogen. The sulphided catalyst comprised 4.6 weight % of nickel, 5.5 weight % of sulphur, and 15 weight % of gamma-alumina, the remainder being hydrogen mordenite having a SiO_2/Al_2O_3 mole ratio of 60/1. The material had an average crush strength of 14 pounds as determined employing a Chatillon Crush Strength Tester.

EXAMPLE 3

460 grams of commercially available hydrogen mordenite powder comprising 8.9 weight % of Al_2O_3 , and 81.1 weight % of SiO_2 , and having a SiO_2/Al_2O_3 mole ratio of 16/1 was impregnated with 250 cc of a solution containing 125 grams of $Co(NO_3)_2 \cdot 6H_2O$. The material was dried at 130 to 140°F for 16 hours.

368 grams of $Al_2(SO_4)_3 \cdot 18H_2O$ were dissolved in 3 litres of distilled water and 300 cc of concentrated ammonium hydroxide were added in order to precipitate aluminium hydroxide. The precipitate was recovered by filtration and washed three times with distilled water.

669 grams of the cobalt-impregnated hydrogen mordenite, were mixed with 971 grams of the wet hydrated alumina gel and passed through a Colloid Mill to effect homogeneous mixing. After partially drying the mixture at 130 to 140°F for 16 hours, the mixture was ground and sieved to -40 mesh. Sufficient water was added to ensure a good extrusion mix and the material was then extruded into 1/16 inch pellets. The pellets were dried and calcined in the same manner as in Example 2. The catalyst comprised 4.7 weight % of cobalt, and 15 weight % of gamma-

alumina, the remainder being hydrogen mordenite having a SiO_2/Al_2O_3 mole ratio of 16/1, and had an average crush strength of 40 pounds. The catalyst was sulphided in the manner described in Example 2 and had the following calculated composition: 5.0 weight % of cobalt, 2.7 weight % of sulphur, and 15.0 weight % of gamma - alumina, the remainder being hydrogen mordenite, and had a crush strength similar to that of the un-sulphided material.

EXAMPLE 4

(For Comparison)

2000 grams of commercially available sodium mordenite 1/16 inch pellets comprising 7.2 weight % of Na_2O , 12.5 weight % of Al_2O_3 , and 75.0 weight % of SiO_2 , and having a SiO_2/Al_2O_3 mole ratio of 10/1 were acid-leached with 4 litres of 6N HCl for 24 hours at a temperature of 130 to 140°F. The acid was decanted and the solids were washed three times with six litres of hot water and three times with six litres of cold water. The acid-leaching was repeated three more times and the product was washed free of chloride ion, dried at 300°F and calcined at a temperature of 1000°F in dry air. The final acid-leached mordenite comprised 0.07% of Na_2O , 2.3 weight % of Al_2O_3 , and 88.3 weight % of SiO_2 , and had a SiO_2/Al_2O_3 mole ratio of 65/1. 423 grams of the acid-leached mordenite pellets were thereafter impregnated with 200 cc of a cobalt nitrate solution containing 105 grams of $Co(NO_3)_2 \cdot 6H_2O$. After drying on steam plate for 2 hours and at 300°F for 16 hours, the pellets were calcined in dry air starting at 500°F for 1 hour and the temperature was raised in increments of 100°F per hour until a final temperature of 1000°F was reached, whereupon the pellets were calcined at 1000°F for 2 hours in dry air.

The calcined pellets were sulphided at 700°F for 4 hours with H_2S , and the final catalyst comprised 5.5 weight % of cobalt, and 3.4 weight % of sulphur, the remainder being hydrogen mordenite having a SiO_2/Al_2O_3 mole ratio of 65/1. The catalyst had an average crush strength of 4.0 pounds.

EXAMPLE 5

(For Comparison)

340 grams of alumina 1/16 inch pellets were impregnated with 200 cc of a cobalt nitrate solution containing 90 grams of $Co(NO_3)_2 \cdot 6H_2O$. The pellets were dried, calcined and sulphided as in Example 4. The final material had a calculated composition of 4.7 weight % of cobalt, and 2.5 weight % of sulphur, the remainder being alumina, and had an average crush strength of 12.7 pounds. Such a composite catalyst has substantially no activity for disproportionating alkyl aromatic

hydrocarbons of the type that can be treated according to the present invention.

EXAMPLE 6

4000 grams of commercially available sodium mordenite powder comprising 6.86 weight % of Na_2O , 10.2 weight % of Al_2O_3 , and 68.2 weight % of SiO_2 , and having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 11.4/1, were acid-leached with 8 litres of 6N HCl for 24 hours at a temperature of 130 to 140°F. The acid was decanted and the solids were washed three times with four litres of hot water and three times with four litres of cold water. The acid-leaching was repeated a second time and the product was washed free of chloride ion, dried at 300°F and calcined in dry air at a temperature of 1000°F. The final acid-leached mordenite comprised 0.31 weight % of Na_2O , 4.53 weight % of Al_2O_3 , and 90.9 weight % of SiO_2 , and had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 34/1.

1323 grams of the above described acid-leached mordenite were impregnated with 600 cc of a cobalt nitrate solution containing 375 grams of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the impregnated powder was dried for 16 hours at a temperature of 130 to 140°F.

1470 grams of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ were dissolved in twelve litres of distilled water, and 1000 cc of concentrated ammonium hydroxide were added to precipitate aluminium hydroxide. The precipitate was recovered by filtration and washed three times with distilled water.

The cobalt-impregnated acid-leached mordenite was mixed with the wet hydrated alumina gel and passed through a Colloid Mill

to effect homogeneous mixing. After partially drying the mixture at 130 to 140°F for 16 hours, it was ground and sieved to -40 mesh. Sufficient water was added to ensure a good extrusion mix and the material was then extruded into 1/16 pellets. The pellets were dried at ambient temperature for 16 hours, at 130 to 140°F for 8 hours and at 300°F for 16 hours. Thereafter the pellets were calcined in dry air starting at 500°F and the temperature was raised in increments of 100°F per hour until a final temperature of 1000°F was reached, whereupon the catalyst was calcined at 1000°F for two hours.

The calcined catalyst was sulphided at 700°F for 4 hours with hydrogen sulphide and subsequently cooled in a stream of dry nitrogen. The sulphided catalyst comprised 3.5 weight % of cobalt, 7.5 weight % of sulphur, and 15.0 weight % of alumina, the remainder being hydrogen mordenite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio 34/1. The material had an average crush strength of 18 pounds as determined employing a Chatillon Crush Strength Tester.

EXAMPLE 7

The catalysts prepared in Examples 4 to 6 were evaluated to determine their ability to disproportionate alkyl-aromatic hydrocarbons. In this Example, toluene was selected as the feedstock and the results are set out in Table II below. The feedstock employed in the runs reported in Table II comprised 99.8% of toluene and 0.2% of carbon disulphide introduced to disproportionation reactors containing 100 cc of the respective catalysts.

TABLE II

Catalyst, Example	4	5	6
Temperature, °F.	553	557	553
LHSV	2.9	3.3	3.0
Pressure, p.s.i.g.	800	800	800
H_2 /hydrocarbon mole ratio	5.2	4.7	5.3
Product Analysis, wt. percent			
Non-aromatics	0.2	0.1	0.2
Benzene	10.0	0.1	18.7
Toluene	77.1	99.8	56.6
C_8 aromatics	11.8	—	21.5
C_9 aromatics	0.9	—	3.0

From Table II it will be seen that catalyst 5, composed of cobalt sulphide on alumina, leads to substantially no conversion of toluene, and was deemed inactive. The introduction of alumina as a component of a catalyst comprising a Group VIII metal on acid-leached mordenite gave a catalyst (Catalyst 6) far superior to one comprising the Group VIII metal and acid-leached mordenite (Catalyst

4). The conversion of toluene when Catalyst 6 was employed (43.4%) was almost twice as great as when Catalyst 4 was used (23%) under substantially the same conditions of temperature, pressure, space velocity and hydrogen to hydrocarbon mole ratio.

Another material, not shown in Table II, comprising 15 weight % of alumina, the remainder being hydrogen mordenite having a

SiO₂/Al₂O₃ mole ratio of 40/1, gave low toluene conversion (about 15%) at 542°F. Deposition of carbon on the material resulted in rapid deactivation.

in conversion rate, whereas the same catalyst with no metal present is virtually inactive within 24 hours due to carbon deposits.

- 5 When a transition metal hydrogenation component is not present on the catalyst, it is deactivated rapidly due to deposition of coke. The addition of from 0.5 to 10 weight %, preferably 3 to 8% of nickel or cobalt, or of
10 from 0.2 to 2.0 weight % of platinum, palladium, rhodium or ruthenium, reduces the deactivation rate of the catalyst. Catalysts containing approximately 5 weight % of cobalt, present in the sulphided state, have operated
15 for over 300 hours with only a slight loss

EXAMPLE 8

A catalyst composed of 5 weight % of cobalt, 5.5 weight % of sulphur, and 15 weight % of alumina, the remainder being hydrogen mordenite having a mole ratio of 40/1, in the form of 1/8 inch pellets was employed to convert *ortho* - xylene and pseudocumene, each feedstock containing 0.2% of sulphur, present as dimethyl disulphide. Table III summarizes the results.

TABLE III

30	Feed	<i>Ortho</i> - xylene	Pseudocumene
	Temperature, °F	504	506
	Pressure, p.s.i.g.	800	800
	LHSV	2	1.5
	H ₂ /hydrocarbon mole ratio	5.8	8.2
35	Product analysis		
	Cracked (light paraffins)	0.14	0.27
	Naphthenes	0.10	0.24
	Benzene	1.80	0.12
	Toluene	17.39	2.18
40	Ethylbenzene	0.01	—
	<i>p</i> - xylene	12.83	4.04
	<i>m</i> - xylene	31.64	10.10
	<i>o</i> - xylene	14.11	3.40
	<i>p</i> - Ethyltoluene	0.01	0.02
45	<i>m</i> - Ethyltoluene	0.05	0.06
	<i>o</i> - Ethyltoluene	<0.01	<0.01
	1,3,5 - Trimethylbenzene	4.86	15.23
	1,2,4 - Trimethylbenzene	13.60	36.90
	1,2,3 - Trimethylbenzene	1.51	4.42
50	Ethylxylenes	0.07	0.22
	1,2,4,5 - Tetramethylbenzene	0.73	8.51
	1,2,3,5 - Tetramethylbenzene	1.00	11.80
	1,2,3,4 - Tetramethylbenzene	0.14	1.95
55	Ethyltrimethylbenzene	—	0.11
	Pentamethylbenzene	—	0.42

Table III shows that the catalyst possesses high activity and high selectivity for isomerizing and disproportionating polymethylbenzenes. *Ortho* - xylene is isomerized with an approach to chemical equilibrium of over 95%, and disproportionated to benzene, toluene, trimethylbenzenes and tetramethylbenzenes to an extent of about 70% of the theoretical amount of disproportionation. The trimethylbenzenes formed are in the ratio of 7.5:68.2:24 for the 1,2,3 - to 1,2,4 - to 1,3,5 - isomers. This ratio is virtually the same as that predicted from thermodynamics. In isomerizing *ortho* - xylene, virtually no ethylbenzene is formed. In disproportionating *ortho* - xylene, the trimethylbenzenes are selectively formed with very little ethyltoluene produced. The total amount of the three

ethyltoluene isomers in the C₉ aromatic fraction is less than 0.35%. Hence, the trimethylbenzenes may be separated with substantially no contamination from ethyltoluene isomers.

Pseudocumene (1,2,4 - trimethylbenzene) is also isomerized to the other trimethylbenzenes, mesitylene and hemimellitene, and is disproportionated to form toluene, xylenes and tetramethylbenzenes. Again, the aromatic fraction with one more carbon atom, namely the C₁₀ fraction, than the feed material is substantially free of ethylaromatics such as ethylxylenes. Consequently, durene may be readily discovered from the C₁₀ aromatic fraction by crystallization. The ratio of the tetramethylbenzenes formed on disproportionation are 8.8:53.0:38.2 for the 1,2,3,4 - to 1,2,3,5 -

to 1,2,4,5 - isomers. Although close to the thermodynamic ratio, the amount of prehnitene (1,2,3,4 - tetramethylbenzene) is slightly less and the amount of durene (1,2,4,5 - tetramethylbenzene) is slightly greater than what would be expected from chemical equilibrium considerations.

EXAMPLE 9

A catalyst composed of 3.5 weight % of cobalt, 9.5 weight % of sulphur, and 15.0 weight % of alumina, the remainder being

hydrogen mordenite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 34/1, in the form of 1/16 inch pellets was employed to disproportionate ethylbenzene and cumene. The conditions and results are set out in Table IV. In each of the runs, 71 grams of catalyst were employed. In addition, runs A and B used an ethylbenzene feedstock containing 2.3 ml of dimethyl disulphide per litre of ethylbenzene. Runs C and D used a cumene feedstock containing 2.4 ml of dimethyl disulphide per litre of cumene.

TABLE IV

Run	A	B	C	D
Temperature °F	525	573	525	570
Pressure, p.s.i.g.	800	800	800	800
LHSV	2.6	2	2	2
H ₂ /hydrocarbon mole ratio	3.1	3.2	3.6	3.5
Product Analysis, wt. percent				
Non-aromatics	0.6	2.0	0.7	1.9
Benzene	18.0	20.0	17.0	21.3
Toluene	0.2	0.8	0.1	0.1
Ethylbenzene	49.9	48.2	0.4	0.5
Cumene	—	—	42.5	39.8
<i>m</i> - and <i>p</i> - Ethyltoluene	0.3	0.8	—	—
<i>o</i> - Ethyltoluene	trace	0.1	—	—
<i>m</i> - Diethylbenzene	18.4	15.9	—	—
<i>p</i> - Diethylbenzene	8.4	7.3	—	—
<i>o</i> - Diethylbenzene	2.0	1.7	—	—
1,3,5 - Triethylbenzene	0.8	1.7	—	—
1,2,4 - Triethylbenzene	1.3	1.1	—	—
<i>n</i> - Propylbenzene	—	—	4.5	7.2
<i>m</i> - Diisopropylbenzene	—	—	17.0	11.8
<i>o</i> - Diisopropylbenzene	—	—	0.2	0.2
<i>p</i> - Diisopropylbenzene	—	—	12.2	10.2
1,2,4 - Triisopropylbenzene	—	—	0.9	1.6
1,3,5 - Triisopropylbenzene	—	—	0.1	0.2
Unidentified	0.1	0.4	4.4	5.2

As seen in Table IV, half of the ethylbenzene feed is disproportionated to benzene and diethylbenzenes, with very little formation of triethylbenzene or other by-products. The total amount of triethylbenzenes is less than one-third of the amount that would be expected from the degree of primary disproportionation of the ethylbenzene. In addition, the amount of 1,3,5 - triethylbenzene formed is less than the amount of 1,2,4 - triethylbenzene, even though thermodynamic considerations predict that the amount of the 1,3,5 - isomer should be double the amount of the 1,2,4 - isomer. The diethylbenzenes formed are in the ratio expected from thermodynamic considerations.

A similar result is obtained when cumene is disproportionated. Tri - isopropylbenzene formation is suppressed relative to what would be expected from the degree of cumene disproportionation. Likewise, 1,3,5 - tri - isopropylbenzene formation is suppressed relative to 1,2,4 - tri - isopropylbenzene.

It is seen that the shape-selective character of the acid-leached mordenite composite catalyst is advantageous in the disproportionation of ethylbenzene or cumene. Their dialkylbenzene products are more desirable than the trialkylbenzenes, and the composite catalyst suppresses the formation of triethylbenzenes and tri - isopropylbenzenes.

WHAT WE CLAIM IS:—

1. A composite catalyst which comprises
 - (a) Hydrogen mordenite having a silica to alumina mole ratio of from 12:1 to 80:1, said hydrogen mordenite being impregnated with
 - (b) a sulphided metal from Group VIII of the Mendeleev Periodic Table, and
 - (c) said composite catalyst comprising from 10 to 50 weight % of an eta-alumina or gamma-alumina binder.
2. A catalyst as claimed in Claim 1, wherein said Group VIII metal comprises from 0.2

to 10.0 weight % of said composite catalyst.

3. A catalyst as claimed in Claim 1 or 2, wherein said Group VIII metal is nickel or cobalt and comprises from 3.0 to 8.0 weight % of said composite catalyst.

4. A catalyst as claimed in Claim 1 or 2, wherein said Group VIII metal is platinum, palladium, rhodium or ruthenium and comprises from 0.2 to 2.0 weight % of said composite catalyst.

5. A catalyst as claimed in any preceding Claim wherein said alumina comprises from 15 to 30 weight % of said composite catalyst.

6. A catalyst as claimed in any preceding Claim which comprises from 3.0 to 15.0 weight % of a sulphided metal from Group VIB of the Mendeleev Periodic Table.

7. A catalyst as claimed in any preceding Claim, wherein said silica to alumina mole ratio is from 25:1 to 50:1.

8. A method of preparing a catalyst according to any preceding Claim which comprises (a) impregnating said hydrogen mordenite with a Group VIII metal;

- (b) admixing said impregnated mordenite with hydrated alumina;

- (c) calcining the resulting mixture at a temperature up to 1100°F thereby converting said hydrated alumina into an eta - alumina or gamma - alumina binder; and

- (d) sulphiding said Group VIII metal.

9. A method as claimed in Claim 8, wherein said hydrogen mordenite, before Step (b), is additionally impregnated with a Group VIB metal.

10. A method as claimed in Claim 8 or 9, wherein Step (c) is conducted at a temperature of from 850 to 1000°F.

11. A method as claimed in any of Claims 8 to 10, wherein Step (d) is conducted at a temperature of from 400 to 800°F.

12. A method as claimed in any of Claims 8 to 11, wherein hydrogen sulphide is employed in Step (d).

13. A process for the conversion of alkyl-aromatic hydrocarbons which comprises contacting said hydrocarbon with a sulphide compound and a composite catalyst according to any of Claims 1 to 7.

14. A process as claimed in Claim 13, wherein said hydrocarbon comprises alkylbenzenes having from 1 to 5 methyl groups.

15. A process as claimed in Claim 13 or 14, wherein said hydrocarbon comprises alkylbenzenes having from 1 to 4 methyl groups.

16. A process as claimed in Claim 13 or 14, wherein said hydrocarbon comprises one or more of the compounds toluene, xylene, trimethylbenzene, tetramethylbenzene and pentamethylbenzene.

17. A process as claimed in any of Claims 13 to 16, wherein said conversion is under-

taken at a temperature of from 400 to 750°F a space velocity of from 0.1 to 15 liquid volumes per volume of catalyst per hour and a pressure of from 100 to 2000 p.s.i.g.

18. A process as claimed in Claim 17, wherein said temperature is from 450 to 650°F, said space velocity is from 0.5 to 8 liquid volumes per volume of catalyst per hour, and said pressure is from 800 to 1200 p.s.i.g.

19. A process as claimed in Claim 13, wherein hydrocarbon corresponds to the formula:



where R is an alkyl group of from 2 to 16 carbon atoms.

20. A process as claimed in Claim 19, wherein R is an alkyl group of from 2 to 4 carbon atoms.

21. A process as claimed in Claim 19, wherein said hydrocarbon is ethylbenzene, cumene, n - propylbenzene t - butylbenzene or a mixture of n - propyl - and isopropylbenzene.

22. A process as claimed in any of Claims 19 to 21, wherein said conversion is carried out at a temperature of from 350 to 650°F, a space velocity of from 0.1 to 15 liquid volumes per volume of catalyst per hour and a pressure of from 100 to 2000 p.s.i.g.

23. A process as claimed in Claim 22, wherein said hydrocarbon is ethylbenzene or cumene and said temperature is from 450 to 600°F.

24. A process as claimed in Claim 22, wherein R is an alkyl group of from 4 to 16 carbon atoms and said temperature is from 400 to 550°F.

25. A process as claimed in any of Claims 13 to 24, wherein said contacting is conducted in the presence of hydrogen.

26. A process as claimed in Claim 25, wherein said hydrogen is employed in an amount of from 100 to 15000 s.c.f./bbl. of feed.

27. A process as claimed in Claim 26, wherein said amount of hydrogen is from 5000 to 10,000 s.c.f./bbl.

28. A process as claimed in any of Claims 25 to 27, wherein the amount of said sulphide compound is sufficient to provide a mole ratio of hydrogen sulphide to hydrogen of from 3×10^{-4} to 1×10^{-2} in the gas phase over the catalyst.

29. A process as claimed in Claim 28, wherein said mole ratio is from 7×10^{-4} to 5×10^{-3} .

30. A catalyst as claimed in Claim 1 sub-

stantially as herein described with reference to any of Examples 1 to 3 and 6.

- 5 31. A method as claimed in Claim 8 substantially as herein described with reference to any of Examples 1 to 3 and 6.

32. A process as claimed in Claim 13 substantially as herein described with reference to any of Examples 1, 7 and 8.

33. A process as claimed in Claim 13 sub-

stantially as herein described with reference to Example 9. 10

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